III.3 Hydrogen Embrittlement of Structural Steels

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Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Enable data-informed design safety factors for hydrogen pipelines, which impacts both reliability/integrity and cost
- Quantify fatigue crack growth aided by hydrogen embrittlement in pipeline steels, particularly for welds

Fiscal Year (FY) 2015 Objectives

- Complete triplicate measurements to establish reliable fatigue crack growth relationships for X52 friction stir weld (FSW) in 21 MPa hydrogen gas
- Complete fatigue tests on two model iron-carbon steels at two values of frequency and H_2 pressures in collaboration with International Institute for Carbon-Neutral Energy Research (I2CNER)

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Fuel Cell Technologies Office (FCTO) Multi-Year Research, Development, and Demonstration (MYRDD) Plan (Section 3.2.5):

(D) High As-Installed Cost of Pipelines

(K) Safety, Codes and Standards, Permitting

Technical Targets

This project impacts the following technical targets for hydrogen delivery components (Table 3.2.4 of the FCTO MYRDD Plan) related to pipelines for gaseous hydrogen delivery:

- Total capital investment: 695,000 \$/mile (FY 2020)
- Transmission pressure: 100 bar (FY 2020)
- Lifetime: 50 years (FY 2020)

One salient safety and reliability issue for steel hydrogen pipelines is hydrogen embrittlement. For steel pipelines, the central unresolved issue is the pipeline performance under extensive pressure cycling. One of the objectives of this project is to enable safety assessments of steel hydrogen pipelines subjected to pressure cycling through the use of structural integrity models in design codes, e.g., American Society of Mechanical Engineers (ASME) B31.12. This structural integrity analysis can determine limits on design and operating parameters such as the allowable number of pressure cycles and pipeline wall thickness. Accurately specifying pipeline dimensions such as wall thickness also affects pipeline cost through the quantity of material required in the design.

FY 2015 Accomplishments

- Triplicate fatigue testing of X52 FSW pipe was completed in 21 MPa hydrogen gas at load ratio (R) of 0.5 and load-cycle frequency of 1 Hz. Three material regions were tested: base metal, center of FSW, and 15 mm off-center from weld.
- Submission of paper to *International Journal of Fatigue* on the effects of microstructure banding on hydrogen-accelerated fatigue crack growth in X65 base metal.
- Completed fatigue testing of fine- and coarse-grained Fe-C model steels at 10 Hz and R = 0.5 in 5.5 MPa and 34 MPa hydrogen gas.

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INTRODUCTION

Carbon-manganese steels are candidates for the structural materials in hydrogen gas pipelines; however, it is well known that these steels are susceptible to hydrogen embrittlement. Decades of research and industrial experience have established that hydrogen embrittlement compromises the structural integrity of steel components. This experience has also helped identify the failure modes that can operate in hydrogen containment structures. As a result, there are tangible ideas for managing hydrogen embrittlement in steels and quantifying safety margins for steel hydrogen containment structures. Fatigue crack growth aided by hydrogen embrittlement is a well-established failure mode for steel hydrogen containment structures subjected to pressure cycling. This pressure cycling represents one of the key differences in operating conditions between current hydrogen pipelines and those anticipated in a hydrogen delivery infrastructure. The reliability/integrity of hydrogen pipelines in a delivery infrastructure will be assessed using structural integrity models along with measurements of relevant material properties. Such models are commonly used in design codes and standards (e.g., ASME B31.12) and could be enhanced through the derivation of physics-based relationships between fatigue crack growth rates and steel microstructure (in addition to cycle frequency, load ratios, and pressures). Enhancements of these models will increase confidence in their integrity, while also enabling higher-pressure, lower-cost pipelines.

APPROACH

The approach of this project is to apply the enabling capability in materials compatibility in high pressure hydrogen at SNL to measure the fatigue crack growth rates of technologically relevant pipeline steels in hydrogen gas. These properties must be measured for the base materials, but more importantly for the welds, which are likely to be most vulnerable to hydrogen embrittlement. Such measurements are necessary for enabling the application of structural integrity models in design codes. For example, the 2014 ASME B31.12 code for hydrogen pipelines includes a fracture mechanics-based integrity management option, which requires material property inputs such as the fatigue crack growth relationship in hydrogen gas.

Following the establishment of reliable fatigue crack growth relationships for pipeline steel base metal, weld heat-affected zone, and weld fusion zone in hydrogen gas, a secondary approach of this project is to apply analytical techniques such as electron microscopy to define the mechanisms of hydrogen embrittlement for the purpose of developing physics-based predictive models. Such predictive models can provide quantitative insight into the effects of environmental, material, and mechanical variables on hydrogen embrittlement. For example, quantifying the effect of microstructure on hydrogen-accelerated fatigue crack growth can aid in the qualification of line pipe steels and their welds for hydrogen service.

RESULTS

The fatigue crack growth rate (da/dN) versus stress-intensity factor range (ΔK) relationship is a necessary input to structural integrity models applied to steel hydrogen pipelines. One such integrity assessment methodology for steel hydrogen pipelines was recently published in the ASME B31.12 code. The measurement of fatigue crack growth relationships in this task supports the objective of establishing the reliability/integrity of steel hydrogen pipelines and informing appropriate design safety factors in future editions of hydrogen piping codes.

Low-strength line pipe steels such as X52, X60, and X65 were selected for this task because of their stakeholder-recognized relevance for hydrogen pipelines. Generally, lower-strength steels are selected for hydrogen pipelines since these steels are less susceptible to hydrogen embrittlement. Fatigue crack growth testing was previously performed on a gas metal arc welded X65 pipe and the results can be found in the FY 2014 annual report. For FY 2015, a section of X52 pipe containing a FSW was supplied by Oak Ridge National Laboratory for fatigue crack growth testing in hydrogen gas. Friction stir welds represent a lower cost welding technology as compared to conventional arc welding with consumables. A solid-state weld is fabricated by inserting a non-consumable welding tool into the steel and mechanically mixing the metal to form a permanent joint. For the supplied X52 pipe, the outside diameter was approximately 340 mm (13.4 in) with a nominal thickness of 6.35 mm (0.25 in). The pipe contains a friction stir weld in the circumferential direction and is shown in Figure 1. Single edge notched (ESE(T)) specimens

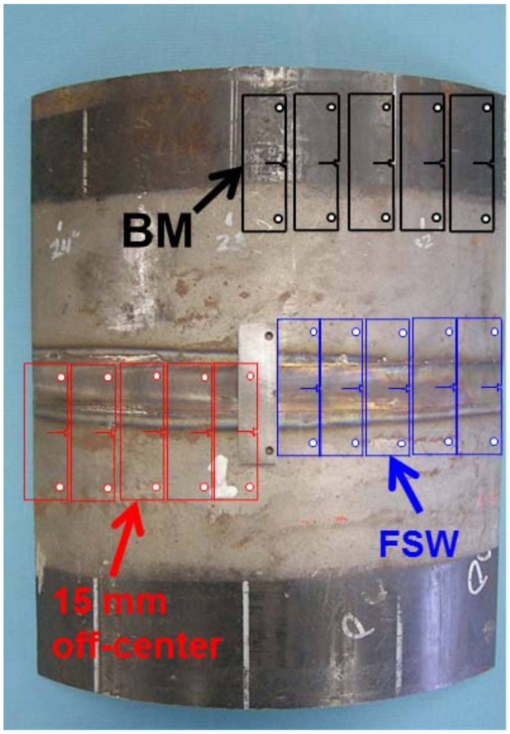

FIGURE 1. Image of the X52 friction stir welded steel pipe with ESE(T) specimens overlaid to show approximate location of specimen machining. Specimens removed from base metal (BM), center of FSW, and 15 mm off-center from FSW.

were extracted in the L-C orientation (wherein load is applied in the longitudinal direction and the crack propagates in the circumferential direction). Three material regions of the pipe were examined: base metal (BM), center of the FSW, and 15 mm off-center from the FSW. The three locations are shown in Figure 1. Figure 2 shows a macro-etch of the FSW. The dashed lines represent the crack planes of specimens tested in the center of the FSW (blue) and the 15 mm off-center position (red). Because specimens were extracted in the L-C orientation, the cracks propagated normal to the image plane in Figure 2. The 15 mm off-center location was chosen to evaluate effects of the welding process on the adjacent base metal (similar to the heat affected zone in studies on the X65 pipe from FY 2014). The location provided sufficient offset from the weld such that the entire crack plane would be contained within a more uniform microstructure, as observed macroscopically in Figure 2. This permitted easier analysis compared to having half of the crack plane located in the FSW and half in the BM.

The results of triplicate fatigue crack growth tests on the X52 friction stir welded pipe in 21 MPa hydrogen gas are shown in Figure 3. The da/dN vs ΔK relationship was measured following ASTM Standard E647 (as specified in ASME B31.12) at R = 0.5. Since the maximum pressure specified for hydrogen gas pipelines in the ASME B31.12 code is 3,000 psi (21 MPa), this upper-bound pressure was selected for the testing. The load-cycle frequency selected for the testing was 1 Hz, consistent with previous testing on line pipe steels and their welds in high pressure hydrogen gas. Fatigue crack growth relationships are plotted in Figure 3 for the three material regions (BM, FSW, and 15 mm off-center from FSW). For comparison, a single test was performed on the BM in air at a frequency of 10 Hz. All specimens tested in 21 MPa hydrogen gas exhibited accelerated fatigue crack growth rates (FCGR) as compared to the test in air and triplicate tests showed good repeatability. The FSW FCGR were slightly higher than the BM whereas the 15 mm off-center results were slightly lower than the BM. Fracture surfaces of select samples were examined in the scanning electron microscope (SEM) at a location corresponding to $\Delta K \sim 8.5$ MPa $m^{1/2}$. Similar fractions of intergranular fracture were observed on fracture surfaces of the BM and off-center specimens, consistent with other fatigue studies [1-4] of ferritic pipeline steels tested in hydrogen gas. However, the fracture surface of the FSW exhibited negligible intergranular fracture. Metallographic samples are under preparation to examine higher magnification SEM imaging of the three material regions examined to identify features in the microstructure that may contribute to the observed FCGR differences.

In collaboration with I2CNER, custom heats of two high-purity Fe-C materials were procured and delivered to Kyushu University (Fukuoka, Japan): a fine-grain-size (15 µm) heat and a coarse-grain-size (70 µm) heat. The goal was to assess the effects of grain size on the onset of hydrogen-accelerated fatigue crack growth. In FY 2014 tests were performed on the two Fe-C alloys at 10 Hz and R = 0.1 in 2.1 MPa H_2. In FY 2015, data from FY 2014 tests were re-analyzed to account for residual stresses, and tests were performed on the two alloys (fine and coarse grain) at a higher load ratio (R = 0.5), frequency = 10 Hz, and two gas pressures = 5.5 MPa (800 psi) and 34 MPa (5,000 psi). These pressures were selected to allow comparisons with data generated from the National Institute of Standards and Technology (NIST), as NIST has developed a phenomenological model based on test results at these two pressures. The preliminary results of the recent tests at higher R ratio are shown in Figure 4 for each alloy (coarse- and fine-grained) at the two gas pressures. Tests were performed in air for comparison. All tests performed

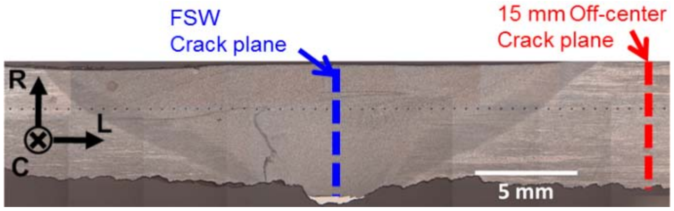

FIGURE 2. Optical image of friction stir welded region is shown with dashed lines representing the approximate location of specimen crack planes in the FSW and 15 mm off-center positions. Base metal samples were extracted more than 100 mm from the FSW.

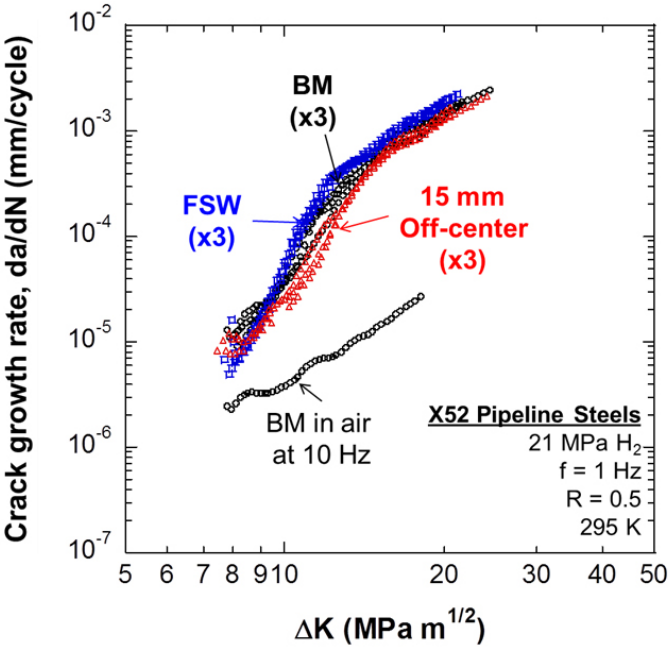

FIGURE 3. Fatigue crack growth relationships (da/dN vs ΔK) of X52 pipeline steel performed in 21 MPa hydrogen gas at R = 0.5 and frequency = 1 Hz. Three material regions were examined: base metal (BM), center of friction stir weld (FSW), and 15 mm off-center to the friction stir weld centerline. BM test in air at 10 Hz is shown for comparison.

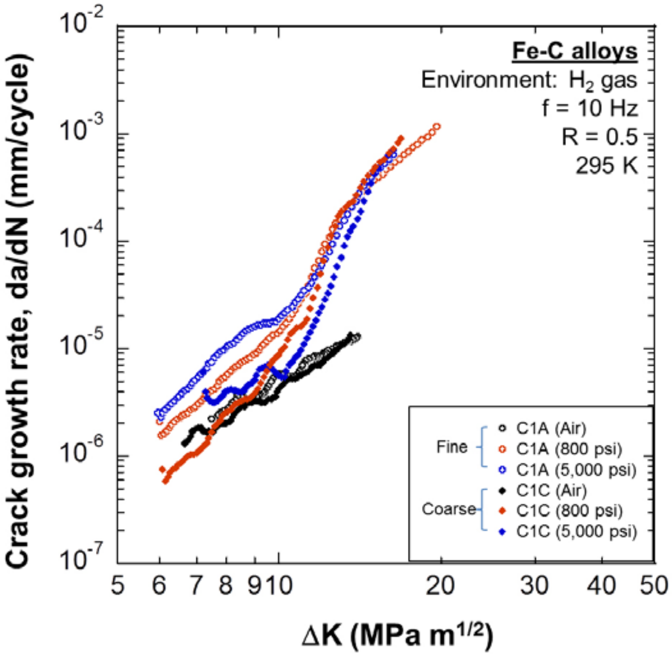

FIGURE 4. Fatigue crack growth relationships (da/dN vs. ΔK) for fine (C1A) and coarse (C1C) grained ferrite-pearlite alloys in 5.5 MPa and 34 MPa hydrogen gas as well as air. Tests were performed at 10 Hz and R = 0.5.

in hydrogen exhibited accelerated fatigue crack growth as compared to the tests in air. The C1A (fine grain) results exhibited greater FCGR when tested at 34 MPa pressure as compared to 5.5 MPa pressure. The C1C (coarse grain) material also exhibited accelerated fatigue crack growth; however, the onset of accelerated FCGR occurred at a lower ΔK for the lower pressure test (5.5 MPa) as compared to the test in 34 MPa hydrogen gas. This is contrary to what was expected as typically higher pressures result in earlier onset of hydrogen-accelerated FCG. Further testing is planned in the form of duplicates and at a lower frequency (1 Hz) to better define the trends.

CONCLUSIONS AND FUTURE DIRECTIONS

- Reliable da/dN vs. ΔK relationships were measured for the X52 friction stir welded (FSW) pipe in 3,000 psi (21 MPa) hydrogen gas. The FSW exhibited slightly greater crack growth rates as compared to the base metal and 15 mm off-center region. However, the results of the base metal indicate that X52 steel is capable of reliable operation in a 100-bar hydrogen pipeline with a thickness no greater than that required for natural gas service.
- Testing of model fine- and coarse-grained Fe-C alloys has commenced at higher R ratio (0.5) at two hydrogen gas pressures (5.5 MPa and 34 MPa) and load-cycle frequency = 10 Hz. Machining of additional specimens is in progress to complete this milestone.
- (Future) Complete manuscript for journal submission on fatigue crack growth testing of friction stir welded pipe in 21 MPa hydrogen gas.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. J.A. Ronevich, B.P. Somerday, C.W. San Marchi, “Effects of Microstructure Banding on Hydrogen Assisted Fatigue Crack Growth in X65 Pipeline Steels.” *International Journal of Fatigue,* submitted July 2015.

2. J. Ronevich and B. Somerday, “Assessing Gaseous Hydrogen Assisted Fatigue Crack Growth Susceptibility of Pipeline Steel Weld Fusion Zones and Heat Affected Zones.” 15th International ASTM/ESIS Symposium on Fatigue and Fracture Mechanics in Anaheim, CA, May 20–22, 2015.

3. “Hydrogen Embrittlement of Pipeline Steels and Welds.” Joe Ronevich and Brian Somerday, presented at ASME B.31.12 Committee Meeting, Atlanta, GA, USA, March 4, 2015.

4. “Hydrogen Embrittlement of Pipeline Steels in Base Metal and Welds,” J. Ronevich and B. Somerday, Joint Delivery-Codes & Standards Tech Team Meeting, Sacramento, CA, January 2015.

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1. C. San Marchi, B.P. Somerday, K.A. Nibur, D.G. Stalheim, T. Boggess, and S. Jansto, “Fracture and Fatigue of Commercial Grade API Pipeline Steels in Gaseous Hydrogen,” presented at the ASME 2010 Pressure Vessels & Piping Division, Bellevue, WA, USA, 2010.

2. B.P. Somerday, P. Sofronis, K.A. Nibur, C. San Marchi, and R. Kirchheim, “Elucidating the variables affecting accelerated fatigue crack growth of steels in hydrogen gas with low oxygen concentrations,” *Acta Materialia,* vol. 61, pp. 6153–6170, 2013.

3. C. San Marchi, B.P. Somerday, K.A. Nibur, D.G. Stalheim, T. Boggess, and S. Jansto, “Fracture Resistance and Fatigue Crack Growth of X80 Pipeline Steel in Gaseous Hydrogen,” presented at the ASME 2011 Pressure Vessels & Piping Division, Baltimore, MD, USA, 2011.

4. S. Suresh and R.O. Ritchie, “Mechanisitic dissimilarities between environmentally influenced fatigue-crack propagation at near-threshold and higher growth rates in lower strength steels,” *Metal Science,* vol. 16, pp. 529–538, 1982.